



Determination of Lead and Cadmium Content of Dill (*Anethum graveolens*) and Onion (*Allium Cepa* L.) Cultivated in Khozestan/Iran

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Abstract

In this study, 60 composite samples of dill and onion from two different cultivated areas in Khozestan province, Iran, were collected and analyzed for the presence and determination of lead and cadmium by flame atomic absorption spectrometry. Samples were burned according to AOAC at 450 °C, and the residue was dissolved in nitric acid. Lead and Cadmium contents were determined using calibration curves at wavelength 217 and 283.8 nm, for Cd and Pb, respectively. In order to evaluate reliability of the results obtained by external calibration curve, standard addition data for a number of randomly selected samples were compared with those of calibration. The results were in good agreements. Two Samples of each vegetable were also spiked with a certain amount of Pb and Cd. The recoveries of standards were in the range of 90-110%. Reproducibility was also good. Mean Cd and Pb concentrations were 0.208, and 1.972 mg.kg⁻¹ dill, respectively. In the case of onion, no lead was detected, but its cadmium content was 0.0475 mg.kg⁻¹. Pb and Cd content of dill were higher than permitted limits reported in Codex.

Keywords: Cadmium; Dill; Lead; Flame Atomic Absorption Spectrometry; Onion.
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1. Introduction

Lead and cadmium are among the toxic heavy metals that are stable in the environment, and their biodegradation does not easily occur [1]. One of the major sources of exposure of humans to heavy metals, such as Cd and Pb is their daily diet [2-4]. People extensively have

vegetables in their daily food basket. Many studies have shown that vegetables are contaminated by Cd and Pb [5, 6]. Medicinal herbs and accordingly their preparations are also polluted by these heavy metals [7, 9].

Cadmium and lead enter agricultural products through contaminated air, soil, and water [10-12], so the level of heavy metals in vegetables and medicinal plants can be a good indication of the extent of pollution in the area. Besides, the health hazards resulting

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Table 1. Lead and cadmium content of dill and onion of Shooshtar and Aghili/ Khozestan province obtained by FAAS. Results are the mean of four measurements.

Sample No.	Dill		Onion	
	Cd	(mg.kg ⁻¹) Pb	Cd	(mg.kg ⁻¹) Pb
1	2.128±0.143	0.130±0.021	0.036±0.001	ND
2	2.066±0.143	0.113±0.002	0.044±0.002	ND
3	2.191±0.094	0.166±0.012	0.052±0.002	ND
4	1.816±0.094	0.201±0.004	0.044±0.003	ND
5	2.190±0.01	0.177±0.012	0.042±0.002	ND
6	2.472±0.090	0.248±0.02	0.044±0.002	ND
7	2.316±0.142	0.251±0.008	0.050±0.004	ND
8	1.653±0.05	0.245±0.145	0.036±0.001	ND
9	1.722±0.093	0.145±0.015	0.039±0.002	ND
10	2.285±0.281	0.246±0.011	0.034±0.002	ND
11	2.145±0.125	0.136±0.020	0.036±0.001	ND
12	2.253±0.235	0.136±0.020	0.058±0.002	ND
13	1.822±0.331	0.207±0.010	0.044±0.002	ND
14	2.065±0.236	0.194±0.002	0.078±0.001	ND
15	1.910±0.281	0.250±0.019	0.053±0.001	ND
16	2.347±0.107	0.133±0.007	0.042±0.003	ND
17	2.776±0.126	0.586±0.05	0.042±0.002	ND
18	1.241±0.016	0.092±0.007	0.048±0.002	ND
19	1.546±0.02	0.092±0.006	0.034±0.001	ND
20	1.426±0.225	0.102±0.007	0.066±0.002	ND
21	2.018±0.126	0.165±0.045	0.039±0.001	ND
22	1.450±0.020	0.151±0.069	0.044±0.001	ND
23	1.454±0.132	0.152±0.006	0.050±0.002	ND
24	1.573±0.011	0.173±0.014	0.058±0.002	ND
25	1.422±0.022	0.199±0.010	0.036±0.001	ND
26	1.675±0.279	0.137±0.010	0.036±0.001	ND
27	1.652±0.012	0.178±0.014	0.036±0.001	ND
28	1.701±0.010	0.187±0.014	0.080±0.003	ND
29	2.868±0.015	0.414±0.012	0.069±0.004	ND
30	2.984±0.120	0.395±0.015	0.058±0.002	ND

ND: Not Detected

from consumption of these agricultural products can be predicted, and reasonable diet can be suggested to prevent food poisoning.

In folk medicine, onion has also been used for whooping cough, chest pain (angina), gallbladder complaints, dehydration, menstrual problems, parasitic infections, and diabetes. It is applied externally for insect bites, wounds, mild burns, warts, boils, and bruises. Its sulfur compound thins the blood and helps prevent dangerous clots while lowering blood pressure and possibly reducing cholesterol levels. Onions also possess the ability to kill a wide variety of germs. And, for asthma victims, the onion extract may even

relieve allergy-induced bronchial constriction.

Dill is a familiar kitchen spice, best known as a flavoring for pickled cucumbers. They act medicinally by relieving spasms and blocking the growth of bacteria. Both dill seed and dill leaf have been used medicinally, but only dill seed has been proven effective. Dill leaf has been used for stomach and intestinal problems, kidney and urinary tract conditions, spasms, and sleep disorders, but its effectiveness for these conditions remains unproven.

Dill and onion in addition to their medical application are extensively used in Iranian diets both in cooked and uncooked forms. Khozestan has a vast cultivation area for these

Table 2. Mean values of Pb and Cd of five randomly selected dill samples obtained by both calibration and standard addition curves.

Lead(mg kg ⁻¹)		Cadmium(mg kg ⁻¹)	
Calibration curve	Standard addition	Calibration curve	Standard addition
2.4±0.12	2.16±0.05	0.25±0.02	0.24±0.02
1.82±0.33	1.93±0.14	0.39±0.02	0.40±0.03
1.43±0.22	1.40±0.03	0.25±0.02	0.26±0.03
1.45±0.13	1.42±0.03	0.41±0.01	0.40±0.02
1.67±0.28	1.64±0.07	0.39±0.01	0.37±0.01

vegetables. Since many environmental sources of pollution are known in Khozestan province, analysis of these agricultural products for the level of pollution seems to be necessary. So in these study vegetables from two cultivated areas, namely Shushtar and Aghili, are analyzed for their Pb and Cd contents.

Different analytical methods are used for the determination of heavy metals in foodstuffs, namely flame and furnace analytical atomic spectrometry [13, 14], stripping voltammetry [15], inductively coupled plasma- time of flight mass spectrometry [16]. Among these, flame atomic absorption spectrometry (FAAS) is simple, and economic but the main limitation on its application is the high detection limits compared to other techniques such as graphite furnace atomic absorption spectrometry and stripping voltammetry.

In this study, reliability of FAAS for determination of lead and cadmium in dill and onion is evaluated. Finally the mean values of these metals in the area are determined.

2. Experimental

2.1. Reagents and materials

All chemicals used in this study were purchased from Merck, Germany. Stock solution of 1000 µg.ml⁻¹ of lead and cadmium were purchased from Chem Lab N.V. (Belgium). Double distilled water was used throughout this study.

2.2. Sample collection

Dill (*Anethum graveolens* L.) and onion

(*Allium Cepa* L.) samples were collected from Shooshtar and Aghili located in Khozestan province. Figure 1 shows sampling positions on the map. For this purpose, 30 farms (15 dill and 15 onion farms) were randomly selected from different locations in agricultural district of Shooshtar and Aghili. Twelve samples were collected from each farm, total of 180 samples. Samples from each farm were divided into two sets of six. Each set were mixed to make composite sample. However, it was two composite samples for each farm and overall of 30 composite samples for dill and the same number for onion. The samples were washed thoroughly with distilled water, cut into pieces, and dried in shadow on a clean place and then grinded. Powders were kept in clean plastic vessels till analysis.

2.3. Sample preparation

The burning procedure was as reported in AOAC [17]. To briefly describe, 15 g powder of each sample was placed in a 50 ml crucible. It was preliminary burned using conventional flame and then transferred to furnace. Furnace was programmed to reach 450 °C, stay at this temperature till a white residue was observed. The residue was dissolved in

Table 3. Mean values of Cadmium of five Onion samples calculated by both calibration and standard addition curves.

Cadmium(mg.kg ⁻¹)	
Calibration curve	Standard addition
0.052± 0.002	0.053±0.001
0.05±0.004	0.05±0.002
0.078±0.001	0.080±0.001
0.058±0.002	0.062±0.001
0.080±0.003	0.082±0.002

Table 4. Recovery of FAAS for the determination of Pb and Cd in dill and onion.

Sample	Lead		Cadmium	
	Found ^a ($\mu\text{g}\cdot\text{ml}^{-1}$)	Recovery%	Found ^b ($\mu\text{g}\cdot\text{ml}^{-1}$)	Recovery%
dill 1 ^c	1.993±0.077	99.90	0.930±0.012	93.00
Dill 2 ^c	2.062±0.138	103.10	1.086±0.011	108.60
Dill 1 ^d	1.818±0.274	90.90	0.916±0.019	91.60
Dill 2 ^d	1.839±0.201	91.95	0.973±0.025	97.30
Onion 1 ^c	-	-	1.070±0.06	107.00
Onion 2 ^c	-	-	1.020±0.08	102.00
Onion 1 ^d	-	-	-	-
Onion 2 ^d	-	-	-	-

a added concentration of Pb was 2 $\mu\text{g}\cdot\text{ml}^{-1}$; b added concentration of Cd was 1 $\mu\text{g}\cdot\text{ml}^{-1}$; c when Pb and Cd standard were separately added to the solutions.; d when both Pb and Cd standards were spiked in a single sample.

minimum amounts of HNO₃, then filtered and made up the solution to the mark in 50 ml volumetric flask. The same procedures were applied to empty crucibles to prepare the blank. Pb and Cd contents of five randomly selected samples were determined by standard addition method and compared with external calibration results. Two samples were spiked with different concentration of standard of these elements. Two samples were simultaneously (both Pb and Cd added) and

separately (two paired samples, one spiked with Pb and one with Cd) spiked with standards and the results were recorded. Precision of the determination were investigated by analyzing randomly selected samples four times in a day and for three consecutive days.

2.4. Apparatus and heavy metal measurement

Flame atomic absorption spectrometer, CTA-3000, Anal. Tech (UK), and Naber



Figure 1. Sampling area of the onion and dill (Iran, Khuzestan province)

Table 5. Reproducibility for determination of lead and cadmium by FAAS.

Sample	RSD% (Cd)		RSD% (Pb)	
	Inter day	Intra Day	Inter day	Intra Day
Dill 1	2.55	9.30	4.08	7.14
Dill 2	2.67	9.66	4.20	6.90
Onion 1	4.21	8.26	-	-
Onion 2	2.32	8.96	-	-

Therm electro-thermal furnace (Germany) were used. All glass wares used in this experiment were soaked in 10% nitric acid for 24 h, then rinsed completely with double distilled water, and dried in an oven before use. Concentrations of Pb and Cd in the 60 samples were determined by FAAS at wavelength of 217 and 283.8 nm for Cd and Pb, respectively.

3. Results and discussions

As determined by pilot studies, the levels of Pb and Cd in dill cultivated in Khozestan province were relatively high and FAAS was suitable for the determination. Only the Pb contents of onions were not in the calibration range of FAAS and cannot be determined by this method without preconcentration. In order to show the reliability of data, accuracy and precision of FAAS method for the determination of Pb and Cd in these vegetables were also evaluated.

Concentrations of Pb and Cd in the 60 samples were determined by FAAS at

wavelength of 217 and 283.8 nm for Cd and Pb, respectively. The results are shown in Table 1. No lead was detected by FAAS in onion samples. In order to check the limit of Pb in onion samples some randomly selected samples were analyzed by graphite furnace but not quantitative amount were detected. It means that the Pb content of onion was even lower than the range of determination of graphite furnace.

In order to evaluate the reliability of the results obtained by the calibration curves, Pb and Cd contents of five randomly selected samples were determined by standard addition method and compared with external calibration results. The results are summarized in Tables 2 and 3. As the results indicate, external calibration can be used as a determination method and no serious matrix effect was seen. To further evaluate the reliability of the results and check the extent of matrix effect, two samples were spiked with different concentrations of standard of these elements. Two samples were

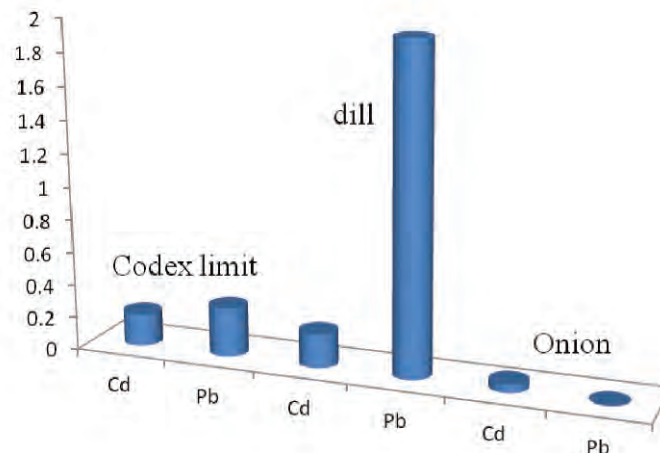


Figure 2. Graphical representation of Pb and Cd content of Khozestan Dill and Onion compared to the limit reported in codex.

simultaneously (both Pb and Cd added) and separately (two paired samples, one spiked with Pb and one with Cd) spiked with standards and the results were recorded. Calibration curve was used to calculate the concentration of unknown and standards. Table 4 shows the results for these kinds of measurements. The recoveries for standards were in the range of 90% to 110%.

Precision of the determination were investigated by analyzing randomly selected samples four times in a day and for three consecutive days. The results have shown good relative standard deviation ranging from 2.5% to 10% for onion and dill (Table 5).

According to results shown in Table 1 and Figure 2, mean values of Pb contents in dill cultivated in Shooshtar were higher than permitted standard limit mentioned in Codex for vegetables (0.3 mg/kg) but Cd level is a bit higher than reported limit (0.2 mg/kg for cadmium). Student's t-test also emphasized that there was significant differences between Pb contents of dill and the codex limit. These contamination levels can be hazardous for consumers and must be controlled carefully. Mean value of Cd in onion is relatively low and far from standard limit mentioned in the Codex as also confirmed by statistical tests.

4. Conclusion

As the results demonstrate, dill samples cultivated in Shooshtar/Khozestan is contaminated by both Cd and Pb. That is mainly due to polluted soil, atmosphere, and irrigation water resulting from so many industrial and urban activities in the province. The main source of onion contamination is contaminated soil and irrigation water. Cadmium contents of soil are relatively high because of uncontrolled use of phosphate, nitrogen and potash fertilizers. So, it is recommended to analyze atmosphere, soil and irrigation water to find a relation between their heavy metals contents and those of agricultural products. Precise diet is also

required.

This study also demonstrates the reliability of FAAS method for the determination of lead and cadmium in above mentioned vegetables.

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